



PATENT SPECIFICATION

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COMPLETE SPECIFICATION

An Improved Catalytic Process

(A communication from STANDARD OIL DEVELOPMENT COMPANY, a corporation duly organized and existing under the laws of the State of Delaware, United States of America, having an office at Linden, New Jersey, United States of America.)

I, JOHN CONRAD ARNOLD, a British subject, of 29, Southampton Buildings, 10 Chancery Lane, London, W.C.2, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:

This invention relates to catalytic reactions, and more particularly, relates to the catalytic conversion of hydrocarbons. In catalytic conversion processes using catalyst particles, such as powdered catalyst, granular catalyst, or other divided catalyst particles, some of the catalyst in finely divided form is carried to the fractionator with the vaporous reaction products by entrainment and is recovered in the bottoms from the fractionator. In some instances, the bottoms from the fractionator with the recovered catalyst have been returned to the reactor but the bottoms form a poor cracking stock and form additional coke or carbonaceous deposits on the catalyst particles. If the bottoms are not returned to the reactor, the catalyst is lost.

In my foreign correspondent's earlier Patent Specification No. 547,048 there is described and claimed a vapor phase catalytic conversion process of the kind in which a suspension of vapors and catalyst is passed through a heated reaction zone, wherein the catalyst is separated from the cracked vapors from the reaction zone by first passing such vapors through a cyclone separator in which the bulk of the catalyst is separated and then passing the vapors through a cooling zone to produce a condensate which is passed in countercurrent to the residual vapors in a second separation zone so as to scrub residual catalyst from such vapors.

It is stated that the catalyst removed from the scrubbing stage may be recovered and used in various ways such as recycled to the reactor for re-use, used in subsequent processing of the bottoms oil or recovered in another cyclone separator after vaporisation in another furnace.

It is also known to recover and recycle catalyst from a cracking operation by condensation of the overhead vapors containing catalyst to form a catalyst slurry in the condensate, the catalyst being mechanically separated from this slurry, e.g. by filtration, and recycled to the cracking stage.

It is also known that the higher boiling products of a catalytic hydrocarbon conversion reaction are, in general, refractory and resistant to further conversion, and that if recycled for further treatment they are apt to cause undue deposition of undesirable carbonaceous deposits on the catalyst in the conversion zone.

The present invention is designed to provide a particularly desirable and economical method of carrying out hydrocarbon conversion reactions continuously in the presence of finely divided catalyst, and makes use of the features set forth above.

Thus the converted vapors from the reactor, together with entrained catalyst, are first subjected to a dry separation step, e.g. in a cyclone separator, in which the bulk of the catalyst is removed. The highest boiling fraction of the vapors is then condensed to form a liquid which is employed to wash the remaining catalyst out in the form of a slurry. Catalyst is continuously separated mechanically from this slurry, the refractory oil being discarded and the separated catalyst being continuously returned to the conversion system, i.e. to the reactor or regenerator.

The present invention accordingly comprises a continuous process for the catalytic conversion of hydrocarbon oils of the type in which the oil vapors are

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- contacted with a finely divided catalyst in a reaction zone, wherein the converted vapors with catalyst particles entrained therein are withdrawn from the reaction 5 zone and subjected to a dry separation step in which the bulk of the catalyst is separated from the vapors and recycled to the conversion system, the vapors containing residual entrained 10 catalyst being passed to a scrubbing zone in which the highest boiling fraction of the vapors is condensed and used to scrub out the residual catalyst with the formation of a catalyst slurry, the catalyst 15 being continuously mechanically separated from the slurry and recycled to the conversion system, and the condensate separated from the slurry being rejected from the system.
- 20 The catalyst is removed from the slurry, preferably either by filtration or by means of a Dorr thickener. It is preferred to recycle at least part of the slurry through the scrubbing zone after 25 cooling it, partly to increase scrubbing efficiency and partly to increase the catalyst concentration in the slurry before recovering the catalyst therefrom. The preferred catalyst concentration in 30 the slurry is 0.5 to 2 lbs./gallon.
- The hydrocarbon conversion reaction is preferably carried out in the presence of a dense bed of fluidised cracking catalyst, which is continuously cycled 35 through a regenerator and back to the reactor. The whole of the catalyst may go overhead with the cracked products and be subjected to the preliminary dry separation step outside the reaction zone, 40 e.g. in a number of cyclone separators in series, or only a minor proportion of the catalyst may be taken overhead with the vaporous products, the contaminated catalyst being continuously withdrawn as 45 a fluidized stream from the lower part of the reaction zone and passed to the regeneration zone. In either case the catalyst recovered from the slurry may be recycled to either the reaction zone or the 50 regenerator, but preferably it is suspended in fresh oil feed and passed to the reaction zone.
- As an alternative to filtration or the use of a Dorr thickener or similar device, 55 the catalyst may be separated from the slurry by settling in a settling zone, preferably maintained at a temperature of 200-500°F., the settled sludge being recycled to the reaction zone. The 60 amount of the refractory oil contained in this settled sludge is sufficiently small for its harmful effect to be negligible.
- In the accompanying drawings,
- Fig. 1 represents one form of apparatus 65 using powdered catalyst in which catalyst is removed from the fractionator bottoms by means of a filter; and
- Fig. 2 represents another form of apparatus using powdered catalyst in which the catalyst is recovered from the fractionator bottoms by means of a Dorr thickener.
- Referring now to the drawings, the reference character (10) designates a line through which liquid or vaporous reactant is passed. The reactant in a hydrocarbon conversion process may be reduced crude, gas oil, heavy naphtha, or other hydrocarbon oil. The hydrocarbon oil may be in vapor form or it may be only partly preheated and partly in vapor form and partly in liquid form. The rest of the heat necessary to vaporise any liquid oil and to raise the oil to cracking or conversion temperature is supplied by powdered catalyst.
- Hot powdered catalyst is introduced into line (10) from line (12) in sufficient amount to effect the desired extent of conversion. In catalytic cracking the catalyst may be acid-treated bentonite clay or synthetically prepared silica-alumina gels, silica gels having magnesia incorporated therein, or other synthetic catalysts. The mixture of reactant and powdered catalyst is passed through line (14) and through distributor plate (16) arranged in a reaction vessel (18). The catalyst is preferably in powdered form having a size of about 200 to 400 mesh or finer but coarser catalyst may be used if desired. When cracking gas oil and when using synthetic silica-alumina gels, a temperature of about 800°F. to 1,100°F. is used and about 3 parts of catalyst to 30 parts of catalyst to 1 part of gas oil by weight are used. The weight of oil per hour per weight of catalyst in the reactor may vary between about 0.5 and 5.0.
- The velocity of the vapors passing upwardly through the reaction vessel (18) is so selected that the catalyst particles become fluidized and the fluidized mixture has a level (22) similar to that of a liquid. When using acid-treated bentonite clay in powdered form, the dense mixture has a density of about 10 lbs./cu. ft. to 30 lbs./cu. ft. in the reaction vessel (18). Above the level (22) the suspension is relatively light and the vapors or reaction products only contain a small amount of entrained catalyst particles.
- The reaction products in vapor form pass upwardly into the separating means (24) arranged in the upper part of the reaction vessel (18). The separating means (24) may be a cyclone separator, Multicloner separator, or the like. The

- reaction products in vapor form still containing some catalyst particles pass overhead through line (26) and into the bottom of fractionating tower (28) which 5 will be further described hereinafter.
- The separated catalyst particles in the separating means (24) are fluidized by the introduction of a fluidizing gas at (32) and the fluidized catalyst particles 10 are returned to the fluidizing mixture in the reaction vessel (18) through line (34) which dips below the level (22) of the catalyst particles therein.
- During the conversion operation the 15 catalyst particles become fouled with carbonaceous deposits or coke. The catalyst particles are withdrawn from the bottom of the reaction vessel through standpipe (36). The bottom of the reaction vessel is provided with gas inlet lines (38) for introducing a stripping gas into the spent catalyst before it is withdrawn from the reaction vessel (18). The stripping gas also serves 20 to maintain the spent catalyst particles in fluidized condition. The spent catalyst particles flow into the standpipe (36) in which they are maintained in a fluidized condition by the introduction of 25 fluidizing gas through line or lines (42).
- The reaction vessel (18) above the dense mixture is maintained under a slight superatmospheric pressure to enable the vaporous reaction products to be passed 30 through the fractionating equipment and associated parts. This pressure plus the pressure developed by the standpipe (36) and the column of relatively dense catalyst in the reaction vessel (18) is sufficient to raise a less dense mixture 35 of the spent catalyst to the regenerator as will be presently described.
- The standpipe (36) is provided with a control valve (44) for controlling the amount of catalyst withdrawn from the reaction vessel (18). A regenerating gas, such as air, or other oxygen-containing gas, is passed through line (46) and mixed with the spent catalyst below the 40 valve (44) to form a less dense mixture of catalyst and air, and this less dense mixture is passed through line (48) into the bottom portion of a regeneration vessel (52). The regeneration vessel (52) 45 is provided with a distribution plate or grid (54) in its lower portion through which the suspension is passed to distribute the regenerating gas and catalyst particles over the area of the regeneration vessel (52).
- The velocity of the regenerating gas is so selected that the powdered catalyst undergoing regeneration is maintained in a relatively dense fluidized condition. 50
- 60 The catalyst in the dense mixture is shown at (56) having a level at (58). In this condition the powdered catalyst assumes many of the characteristics of a liquid. The density of the dense fluidized catalyst is about 10 lbs./cu. ft. to 30 55 lbs./cu. ft.
- The catalyst being regenerated is maintained in the regeneration zone for a sufficient time to effect the desired extent of regeneration. Substantially all of the coke or carbonaceous material is removed from the catalyst particles. The regeneration gases pass upwardly through the dense mixture in the regeneration vessel (52) and into the space above the level (58) to form a disperse phase in which the amount of catalyst suspended in the gases is relatively small. The temperature during regeneration is maintained between about 1,000°F. and 1,200°F. 60
- The regeneration gases containing entrained catalyst particles are passed through a separating means (62) which is arranged in the upper portion of the regeneration vessel (52). The separating means (62) may be a cyclone separator, or any other suitable gas-solid separating device. The separated solid particles are fluidized by 65 the introduction of fluidizing gas at (64) into the hopper (66) of the separating means (62) and the solid particles in fluidized condition are returned to the relatively dense mixture of catalyst in the regeneration zone (52) through line (68) which extends below the level (58) of powdered catalyst or solid material in the regeneration zone (52).
- Regeneration gases containing entrained solid particles leave the top of the regeneration zone (52) through line (72) and are passed through a heat exchanger (74) before being passed to an electrical precipitator (76). The heat exchanger (74) may be a waste heat boiler or any other form of heat exchanger. The regeneration gases at a lower temperature are passed through line (78) to the electrical precipitator (76) in which there is an additional separation of powdered material. The powdered material is collected in a hopper (82) and passed to a standpipe (84) from which it can be returned to the regeneration vessel (52) or to the reaction vessel (18) in any desired manner. The regeneration gases substantially free of powdered material are passed to the atmosphere through line (86). 70
- Returning now to the regeneration vessel (52), it will be noted that the regeneration vessel is placed at a higher level than the reaction vessel (18). Regenerated catalyst in fluidized condition 75

is withdrawn from the body of catalyst undergoing regeneration shown at (56) through a funnel-shaped member (88) which extends above the distribution plate 5. From the funnel-shaped member (88) the fluidized catalyst flows into a standpipe (92) having a control valve (94) at its lower end. The control valve (94) controls the amount of catalyst 10 being passed to line (12) for admixture with the reactant passing through line (10) as above described.

The hot regenerated catalyst in the standpipe (92) is maintained in a fluidized condition by the introduction of a fluidizing gas, such as air, through lines (96) which are spaced along the length of the standpipe (92). The standpipe (92) forms a column of fluidized solids producing a hydrostatic pressure at its lower end and this pressure plus the head of fluidized material (56) in the regeneration zone (52) is sufficient to return the regenerated catalyst to the 25 reaction vessel (18).

Returning now to the fractionating tower (28), the vaporous reaction products containing entrained catalyst are passed through line (26) into the 30 scrubbing section (102) in the bottom of the fractionating tower (28). The vaporous reaction products are cooled and heavier constituents are condensed therefrom. In addition, a scrubbing oil 35 is introduced into the upper part of the scrubbing section through line (104). In a hydrocarbon cracking process the temperature of the scrubbing section is about 550°F. to 650°F. The vapors enter 40 at about 900-975°F. The vapors are cooled to the scrubbing temperature by the scrubbing oil. All of the entrained powdered catalyst is scrubbed out of the vapors in the scrubbing section (102).

45 The uncondensed vapors are passed upwardly through the fractionating section (106) of the fractionating tower (28) and desired products are separated. The lightest vapors pass overhead through line (108) and cooler (110) to condense normally liquid hydrocarbons. The cooled and condensed material is passed to a separator (112) for separating liquid from gases. The gases 50 pass overhead through line (114) and the liquids, which in this case contain gasoline constituents, are withdrawn through line (116).

If desired, a portion of the liquid 60 passing through line (116) may be returned to the upper part of the fractionating section (106) through line (118) as reflux or other refluxing liquid may be introduced through line (118).

65 Further down the fractionation tower a

sidestream is withdrawn through line (122) which comprises a heating oil. Further down the fractionating tower another side stream is withdrawn through line (124) and this side stream comprises cycle gas oil which may be recycled to the reaction vessel (18). Higher boiling constituents from the fractionating system (106) flow down into the scrubbing section (102).

The bottoms in the scrubbing section (102) contain the recovered catalyst in a slurry and this slurry is withdrawn through line (132) from the bottom of the scrubbing section. This oil from the bottom of the scrubbing section contains highly refractory stock which is not suitable as cracking stock. If this stock is returned to the reaction vessel (18), it results in an increased deposition of coke or carbonaceous material on the catalyst particles without the production of a large amount of gasoline. Therefore it is not desirable to recycle this heavy refractory oil to the reaction vessel (18) but it is desirable to recover the catalyst which is suspended in the bottoms oil.

A portion of the bottoms oil containing catalyst is passed through line (132) by pump (134) and through heat exchanger (136) for return through line (104) as the scrubbing oil for the scrubbing section (102) in the fractionating tower (28). The heat exchanger (138) may be a waste heat boiler or any other suitable heat exchanger. This cool oil acts to cool the reaction vapors introduced through line (26) and to condense heavier constituents from the reaction products, and also functions to increase the concentration of catalyst particles suspended in the bottoms oil by recycling. When the desired concentration of catalyst is obtained in the bottoms oil, at least part of the oil is passed through line (138) at a temperature of about 600-650°F. and heat exchanger (140) and then to a filter (142) for separating catalyst particles from oil. In the heat exchanger (140) the temperature of the oil slurry is reduced to about 350°F. The filter is preferably operated continuously. The concentration of catalyst in the oil in line (138) is about 0.5 lb. per gallon to 2.0 lbs. per gallon.

The filter (142) may comprise any suitable filter, such as a vacuum filter or a filter press, or the like. Preferably a continuous filter, such as a rotary filter, is used. With a rotary filter the drum is precoated with fresh catalyst and the filtered catalyst is washed while it is on the drum. Or a Sweetland filter may be used. The separated oil is passed through line (144) to storage and the recovered

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catalyst particles are withdrawn through line (146).

The separated catalyst may be picked up in a gas stream and returned to the reaction vessel (18) or the regeneration vessel (52). Preferably the recovered catalyst is introduced into a mixing vessel (148) provided with a stirrer (152) and oil feed is introduced into the vessel (148) through line (154) to dilute the catalyst slurry. A slurry of catalyst and oil is produced in the container of vessel (148) which is withdrawn from the bottom through line (156) and passed through this line by pump (158). The oil slurry is preferably passed to the regeneration zone (52) into the body of catalyst (56) or it may be passed through line (162) into the feed line (10) for introduction into the reaction vessel (18).

Instead of using a filter for separating the catalyst from the bottoms taken from the fractionator (28), other separating means may be used, such as a centrifuge, a Dorr thickener, etc. If desired, the oil bottoms may be mixed with a relatively light hydrocarbon oil, such as naphtha or light gas oil, to remove tarry deposits from the catalyst particles and to facilitate removal of the particles from the oil bottoms.

The form of the invention shown in Fig. 2 will now be described. In Fig. 2 the reaction and regeneration vessels are of a slightly different construction in that the vapors or gases and catalyst particles pass overhead with these vapors rather than having the catalyst particles drawn off from the bottom of the vessels as a dense phase. Also, in Fig. 2 there is shown a Dorr thickener for separating catalyst from oil bottoms withdrawn from the bottom of the fractionator.

The reactants are passed through line (202) and mixed with catalyst particles from line (204) and the mixture is passed through line (206) to the bottom of the reaction vessel (208). The reaction vessel (208) has a bottom distribution plate (212) through which the mixture is passed and distributed across the area of the reaction vessel. In the conversion of hydrocarbon oils, partly preheated hydrocarbon liquids or heated hydrocarbon vapors are passed through line (202). If partly heated liquids are used, a sufficiently large amount of hot catalyst particles is used to vaporize the liquid reactants and raise them to the conversion temperature desired. When catalytically cracking a relatively heavy hydrocarbon oil, such as gas oil, and when using a catalyst, such as acid-treated bentonite or synthetic silicalumina gels or the like, about 2 parts

of catalyst to one of oil by weight to 20 parts of catalyst to one of oil may be used, and the temperature during cracking is about 800°F. to 1,100°F. Preferably the catalyst particles have a size between about 200 to 400 standard mesh or finer. The weight of oil per hour per weight of catalyst in the reaction vessel may vary between about 0.5 and 5.0

The velocity of the reactants in gaseous form passing through the reaction vessel (208) is controlled to obtain some settling of the particles in the reaction vessel (208) with respect to the reactants but complete settling out is avoided. The catalyst particles become fluidized and the mixture is relatively dense, having a density of about 10 lbs./cu. ft. to 25 lbs./cu. ft. when using powdered acid-treated bentonite as the catalyst. The fluidized particles assume a level (213) similar to that of a liquid.

Above the dense phase there is a light phase (214) which is a relatively light suspension of catalyst particles in a gaseous fluid. In this form of the invention all of the vaporous or gaseous reaction products pass overhead from the reaction vessel (208) and all of the catalyst passes overhead with the reaction vapors or gases. The mixture of vapors or gases and powdered catalyst leaves the top of the reaction vessel (208) through line (216) and is preferably passed through separating means to separate the bulk of the catalyst particles from the reaction vapors or gases.

As shown in the drawing, three cyclone separators are used but other separating means may be used, if desired. The mixture passes into the first separator (218) in which a large part of the entrained catalyst particles is separated. The gases or vapors then pass through line (222) to a second cyclone separator (224) in which there is an additional separation of catalyst particles from gases or vapors. The gases or vapors then pass through line (226) into a third cyclone separator (228) to separate additional catalyst particles from vapors or gases.

The separated vapors or gases still contain some entrained catalyst particles and these gases or vapors are passed through line (232) into a fractionating tower (234) as will be hereinafter described in greater detail. The catalyst particles separated in the cyclone separators are passed to a hopper (236). Cyclone separators (218), (224) and (228) are provided respectively with dip pipes (238) (242) and (244) for returning the separated catalyst particles to the hopper (236) and below the level (246) of catalyst particles therein. Line (248)

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- is provided in the top of the hopper (236) for removing gases or vapors from the hopper (236) and for leading them to the outlet line (222) from the first cyclone separator. Aerating lines (252) are provided at the bottom of the hopper (236) for introducing fluidizing or aerating gas to maintain the catalyst particles in the hopper in a dry fluidized condition.
- The fluidized spent catalyst particles flow into a standpipe (254) provided with a control valve (256) at its lower end. Preferably aerating gas is introduced through lines (258) at spaced intervals along the length of the standpipe (254) to maintain the catalyst particles in a fluidized condition so that a column of fluidized particles is provided which produces a hydrostatic pressure at its lower end. The standpipe (254) is of sufficient height to produce a sufficient hydrostatic pressure for moving the catalyst particles through the regeneration system presently to be described.
- Regenerating gas, such as air or oxygen-containing gas, is passed through line (262) and is mixed with spent catalyst particles passing through the control valve (256) from the standpipe (254). The mixture is passed through line (264) and into the bottom of the regeneration vessel (266) below distribution plate (268) therein. The velocity of the regenerating gas in the regeneration vessel (266) is so controlled that the catalyst undergoing regeneration is maintained in a dry fluidized condition and has a level indicated at (272).
- When using acid-treated bentonite clay, the density of the mixture in the regeneration zone or vessel is about 10 lbs./cu. ft. to 25 lbs./cu. ft. The catalyst particles are maintained in the regeneration vessel (266) for a time sufficient to substantially completely burn off fouling material from the catalyst particles. In a catalytic cracking operation coke or carbonaceous material is deposited on the catalyst particles during the cracking operation and this coke or carbonaceous material is burned from the catalyst particles during regeneration.
- It is necessary to control the temperature during regeneration to prevent overheating of the catalyst particles. This may be done by providing a heat exchanger (not shown) in the regeneration vessel (266) or part of the catalyst particles being regenerated may be removed from the regeneration vessel, cooled and returned to the regeneration vessel (266). The temperature during regeneration is about 1,000°F. to 1,200°F.

Above the dense phase (272) in the regeneration vessel (266) is a less dense or light phase (274) which comprises a light suspension of catalyst particles in regeneration gases. In this form of the invention the regenerated catalyst particles and the regeneration gases all go overhead from the regeneration vessel (266) through line (276) to separating means which comprises a series of cyclone separators. These cyclone separators function to remove most of the regenerated catalyst particles from the regeneration gases. The system of cyclone separators is similar to that shown in connection with the reaction vessel (208) and will be only briefly described. Cyclone separators (278), (282) and (284) are provided in series.

Line (286) connects the outlet of the first cyclone separator with the inlet of the second cyclone separator. Line (288) connects the second separator with the third cyclone separator. Dip pipes (292), (294) and (296) are provided respectively for cyclone separators (278), (282) and (284). A line (298) is provided for connecting the top of the hopper (302) with the outlet line (286) from the first cyclone separator (278). The dip pipes (292), (294) and (296) dip below the level (304) of catalyst particles in the hopper (302).

The regenerated catalyst particles in the hopper (302) are maintained in a fluidized condition by fluidizing gas introduced into the bottom of the hopper through lines (306). The fluidized regenerated catalyst particles at a temperature of about 1,000°-1,200°F. are introduced into standpipe (308) which is provided with fluidizing lines (312) along its length for introducing fluidized gas to maintain the regenerated catalyst particles in fluidized condition in the standpipe.

In this way a column of fluidized particles is produced which exerts hydrostatic pressure at the base of the standpipe. The standpipe (308) is provided with a control valve (314) for controlling the amount of regenerated catalyst particles being introduced into line (204) above described. Fresh catalyst may be introduced through line (316) into hopper (302) to replace catalyst lost during the operation of the process.

The regeneration gases leave the last separator (284) through line (318) and still contain entrained catalyst particles. The regeneration gases are cooled by being passed through heat exchanger (322) which may be a waste heat boiler and the cooled gases are then passed to an electrical precipitator (324) for separ-

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ating entrained catalyst particles from the regeneration gases.

The regeneration gases are vented to the atmosphere through line (326). The separated catalyst particles collect in the bottom of the precipitator (324) and are introduced into standpipe (328) provided with fluidizing lines (332) for introducing fluidizing gas into the standpipe (328) at spaced intervals. The catalyst particles recovered in the precipitator (324) are extremely fine and are difficult to fluidize. Preferably some of the coarser catalyst particles from the hopper (302) are introduced into the bottom of the electrical precipitator to produce a mixture of catalyst particles which is more easily fluidized.

The standpipe (328) is provided with a control valve (334) for controlling the rate of withdrawal of the catalyst from the standpipe (328). A carrier gas, such as air, is passed through line (336) and is mixed with the catalyst particles below control valve (334) and this mixture is passed through line (338) to any desired part of the system. Preferably the mixture in line (338) is introduced into the tertiary cyclone on the regenerator (284).

Returning now to the vaporous reaction products passing through line (232) to the fractionating tower (234), the vaporous reaction products are introduced into a scrubbing section (342) at the bottom of the fractionating tower (234). Scrubbing oil is introduced into the top of the scrubbing section through line (344). Heavier constituents are condensed from the reaction products and these, together with the scrubbing oil, scrub out residual catalyst particles from the vaporous reaction products. In the catalytic conversion of hydrocarbons, the higher boiling constituents will be relatively high boiling hydrocarbons. The relatively higher boiling hydrocarbons, together with catalyst, are withdrawn from the bottom of the scrubbing section (342) through line (346) and are further treated as will be presently described.

Uncondensed vapors and gases leave the top of the fractionating tower (234) through line (348) and are passed through a condenser (352) and then to a separating vessel (354) for separating liquids from gases. The gases pass overhead through line (356) and the liquid 60 is withdrawn through line (358) from the bottom of the separating vessel (354). When cracking heavier hydrocarbons, the liquid withdrawn through line (358) comprises a light hydrocarbon liquid containing gasoline constituents.

Reflux liquid is introduced into the top of the fractionating tower through line (362). Any suitable reflux liquid may be used from an extraneous source or a part of the liquid passing through line (358) may be returned to the top of the fractionating tower as reflux liquid.

A side stream comprising a higher boiling liquid may be withdrawn through line (364) from the fractionating tower (234). Another side stream may be withdrawn from the fractionating tower (234) through line (366) from a lower point in the fractionating tower. When cracking hydrocarbons, the liquid withdrawn through line (364) comprises a heating oil and the heavier fraction withdrawn through line (366) comprises cycle gas oil which may be returned to the reaction vessel (208) for further cracking.

The heavier oil or bottoms withdrawn through line (346) from the bottom of the scrubbing section (342) is pumped through the line by pump (368). In order to build up the concentration of the catalyst particles in the scrubbing section of the fractionating tower, at least part of the bottoms withdrawn from the scrubbing section (342) is passed through line (372) and cooler (374) and then returned to the top of the scrubbing section through line (344). When the desired concentration of catalyst particles in the bottoms is obtained, at least part of the bottoms is passed through line (376) to a Dorr thickener (378). The concentration of catalyst particles in the oil bottoms in line (376) in a catalytic conversion process is about 0.5-2.0 lbs./gallon. A heat exchanger may be provided in line (376) for controlling the temperature of the slurry going to the thickener (378).

The bottoms liquid is introduced into the central upper part of the Dorr thickener (378). A stirrer (382) is provided having rakes (384) at its lower end in the Dorr thickener (378). Preferably the bottom of the thickener is cone-shaped as shown at (386) to permit withdrawal of the heavy sludge from the bottom of the Dorr thickener.

The temperature of the oil bottoms in the Dorr thickener (378) is maintained between about 200°F. and 500°F. in order to obtain the best operation. The temperature selected varies with the viscosity of the oil. High enough temperatures are selected to give a sufficiently low viscosity so that rapid settling is obtained. The bottoms oil being introduced into the Dorr thickener should be about the same temperature as the oil

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in the thickener to avoid thermal currents being set up.

In the Dorr thickener the catalyst particles settle out and form a sludge 5 (388) shown in the drawing by the darker shading in the Dorr thickener (378). The upper layer (392) is the clarified oil and the amount of catalyst particles in this oil should be maintained at below about 10 0.01 lb./gallon of oil. The clarified oil is withdrawn through line (394) and passed to storage but is not recycled to reaction vessel (208) because it is an extremely poor cracking stock. The 15 clarified oil withdrawn through line (394) is about three-fourths of the oil sent to the Dorr thickener.

The heavy sludge of catalyst particles 20 in the heavy oil has a concentration of about 1.5 lbs/gallon of oil to 6 lbs./gallon of oil. This sludge is withdrawn from the bottom of the Dorr thickener through line (398) and is passed through the line by pump (398). The heavy sludge 25 may be returned through line (402) to the oil feed line (202) for return to the reaction vessel (208). Or the sludge may be passed through line (404) to the regeneration vessel (266) 30 to regenerate the catalyst particles. Preferably the sludge is mixed with fresh feed before being passed to the reactor or regenerator to about one pound of catalyst to one gallon of oil so that the 35 resulting oil will be easier to pump.

The heavy oil withdrawn from the bottom of the fractionator through line (346) is a poor cracking stock and it is preferably withdrawn from 40 the system. However, it is desirable to recover the catalyst particles from the oil, and according to this invention, the catalyst particles are separated from the oil before being returned 45 to the system. The oil is withdrawn through line (394) and may be passed to storage or otherwise disposed of.

If the heavy oil withdrawn from the bottom of the fractionating tower (234) 50 through line (346) is returned to the reaction vessel (208), exceedingly large amounts of coke are laid down on the catalyst particles and large amounts of gas are produced without the production 55 of much gasoline. The following data show the improvement obtained by withdrawing the bottoms oil from the system rather than circulating it back to the reaction vessel:

60 In a commercial fluid catalyst cracking unit employing a synthetic silica-alumina gel type of catalyst and operating at a feed rate of 12,000 barrels per day, a conversion of 65% of the feed to

other products was obtained with a light paraffinic gas oil feed at a temperature of 975°F. In this operation 820 barrels per day of the slurry of catalyst and fractionator bottoms was recycled to the reactor. Under these conditions 5.5% of the gas oil feed was converted to coke which had to be removed from the catalyst by regeneration. When a slurry settler of the type described with reference to Fig. 2 was installed with fresh feed used to dilute the settled slurry for recycle to the reactor but with other conditions remaining unchanged, the conversion of fresh feed to coke was reduced to 4.5% on the feed.

In the form of the invention shown in Fig. 2, it is to be understood that instead of using a Dorr thickener, other separating means may be used, such as filter, a centrifuge, such as a Laughlin centrifuge, or the like. The filtering arrangement shown in Fig. 1 may be used instead of the Dorr thickener shown in Fig. 2. If desired, a relatively light hydrocarbon oil, such as naphtha or light gas oil, may be mixed with the oil slurry passing through line (378) or into the slurry in the Dorr thickener (378). The naphtha tends to dissolve tarry substances from the catalyst particles and also assists in settling of the catalyst particles. The naphtha may be recovered from the clarified oil passing through line (394) by distillation.

Instead of using only one Dorr thickener, two thickeners may be used in series with a washing step between the two thickeners. Fresh oil feed may be used as a wash oil or heavy cycle oil from line (386) in Fig. 2 may be used. Also the combination of a Dorr thickener with a filter or the combination of a Dorr thickener with a centrifuge may be used so that the bulk of the liquid is removed in the Dorr thickener before the slurry is passed to the filter or the centrifuge.

While the invention has been described in connection with the cracking of higher boiling hydrocarbons, it is to be understood that other hydrocarbon conversion operations are contemplated in which finely divided catalyst is used. The invention may be used in catalytic reactions generally where solid catalyst is used in powdered or granular form, whether moving or stationary, where finely divided catalyst is entrained in vaporous or gaseous products leaving the reaction zone, but the invention is especially useful in hydrocarbon conversion processes where catalyst particles are collected in refractory oil.

While two forms of the invention have been shown and others have been des-

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cribed, it is to be understood that these are only by way of example.

Having now particularly described and ascertained the nature of the said invention and in what manner the same is to be performed, as communicated to me by my foreign correspondents, I declare that what I claim is:—

1. A continuous process for the catalytic conversion of hydrocarbon oils of the type in which the oil vapors are contacted with a finely divided catalyst in a reaction zone, wherein the converted vapors with catalyst entrained therein are withdrawn from the reaction zone and subjected to a dry separation step, in which the bulk of the catalyst is separated from the vapors and recycled to the conversion system, the vapors containing residual entrained catalyst being passed to a scrubbing zone in which the highest boiling fraction of the vapors is condensed and used to scrub out the residual catalyst with the formation of a catalyst slurry, the catalyst being continuously mechanically separated from this slurry and recycled to the conversion system, and the condensate separated from the slurry being discarded from the system.
2. A process according to Claim 1, wherein the catalyst is removed from the slurry by filtration or by means of a Dorr thickener.
3. A process according to Claim 1, wherein the catalyst is separated from the slurry by settling in a settling zone, preferably maintained at a temperature of 200-500°F., the settled sludge being recycled to the reaction zone.
4. A process according to any of the preceding claims, wherein the slurry is cooled and at least partially recycled

through the scrubbing zone, whereby improved scrubbing is obtained and the catalyst concentration in the slurry is increased.

5. A process according to any of the preceding claims, wherein the catalyst concentration in the slurry is from 0.5 to 2 lbs. per gallon.

6. A process according to any of the preceding claims, wherein the conversion reaction is carried out in the presence of a dense bed of fluidized cracking catalyst, which is continuously cycled through a regenerator and back to the reactor.

7. A process according to Claim 6, wherein the whole of the catalyst is taken overhead with the converted vapors and subjected to separation in a series of cyclone separators, the separated catalyst being passed to the regenerator.

8. A process according to Claim 6, wherein a minor proportion of the catalyst is taken overhead with the converted products, contaminated catalyst being continuously withdrawn as a fluidized stream from the lower part of the reaction zone and passed to the regenerator.

9. A process according to any of the preceding claims, wherein the catalyst recovered from the slurry is suspended in fresh hydrocarbon oil feed and passed to the reaction zone.

10. A process according to any of the preceding claims, wherein the hydrocarbon oil feed is a gas oil.

Dated this 9th day of October, 1944.

D. YOUNG & CO,
29, Southampton Buildings,
Chancery Lane, London, W.C.2,
Agents for the Applicant.

FIG. 1.

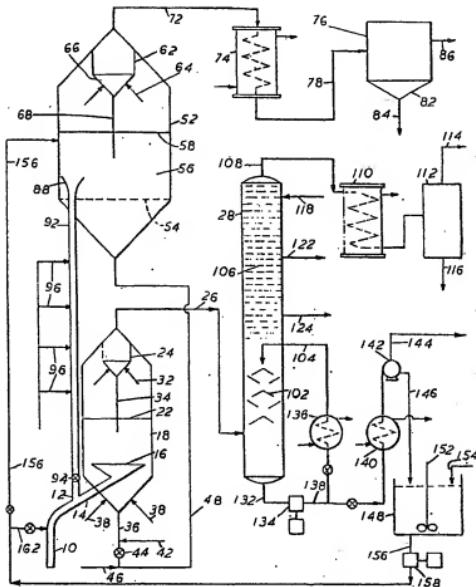
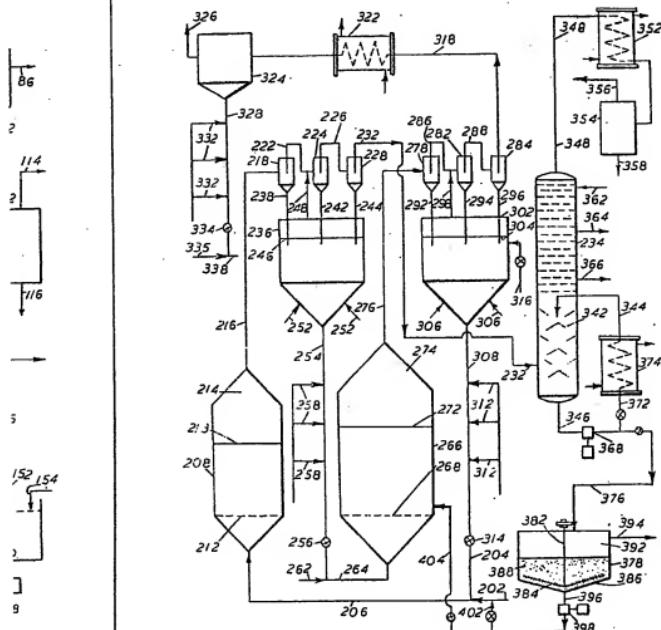


FIG. 2.



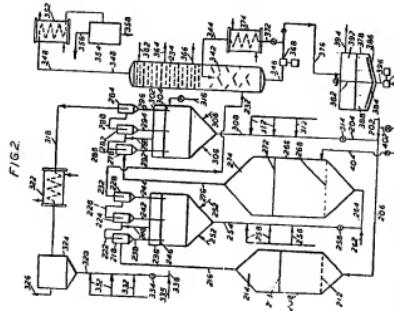
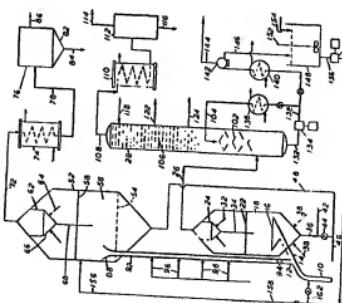
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